

# Electrochromic Sensor for Hydrogen-Phosphate Ion with Spinel-Type Oxide-Based Thin-Film Electrode

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## INTRODUCTION

Detection of exact amount of hydrogen-phosphate ion has been becoming very important for the protection of global environment. So far, many kinds of compact hydrogen-phosphate ion sensors, such as ion-selective electrodes (ISEs) [1], bio-related systems, and amperometric sensor devices [2] have been investigated. However, they have some problems with respect to sensitivity, selectivity, stability, and sensing conditions for the practical applications. Recently, we have developed opto-electrochemical hydrogen-phosphate ion sensors based upon electrochromic reaction of metal oxides ( $\text{Co}_3\text{O}_4$ ,  $\text{NiO}$ ) [3,4]. Here, we report on the sensing properties of the electrochromic-type hydrogen-phosphate ion sensors based on Co-/Ni- based spinel-type oxide thin-film electrodes.

## EXPERIMENTAL

Spinel-type oxide thin-film electrodes ( $\text{MnCo}_2\text{O}_4$ ,  $\text{NiCo}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ ,  $\text{Co}_2\text{CrO}_4$ ,  $\text{Ni}_2\text{CrO}_4$  etc.) were prepared by a spin-coating method. Organic solutions of ethanol with metal octylates or aqueous solutions of metal nitrates with poly (vinyl alcohol) (PVA) or poly (vinyl pyrrolidone) (PVP) were spin-coated onto indium-tin-oxide (ITO:  $10 \Omega/\text{sq.}$ ) glass substrates, dried at  $150^\circ\text{C}$ , and then calcined at  $450^\circ\text{C}$  for 2 h. The products were characterized by means of XRD, FE-SEM, AFM, etc.

Electrochemical and optical properties of these oxide thin-film electrodes for sensing hydrogen-phosphate ion were investigated at room temperature in a quartz electrochemical cell which was placed in a spectrophotometer and connected to a potentiostat. An Ag/AgCl and a Pt-wire were used as a reference and a counter electrode, respectively. A sample solution was prepared by mixing  $\text{K}_2\text{HPO}_4$  with 0.1 M ammonium acetate-ammonia buffer solution adjusted to pH = 9.3.

## RESULTS AND DISCUSSION

### Preparation of spinel-type oxide thin-film

Spinel-type oxide thin-films of  $\text{MnCo}_2\text{O}_4$ ,  $\text{NiCo}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$  could be prepared on ITO glass substrates from their metal-octylates at  $450^\circ\text{C}$ . While, those of  $\text{Co}_2\text{CrO}_4$  and  $\text{Ni}_2\text{CrO}_4$  could be obtained from their metal nitrates with addition of PVA (7.5wt%) or PVP (1wt%) aqueous solution. X-ray diffraction analysis of the obtained thin-films revealed that the oxide thus prepared exhibited well-crystallized and almost single-phase spinel-type oxide. SEM observation of the  $\text{MnCo}_2\text{O}_4$  thin-film revealed that the surface of the film was relatively smooth and consisted of fine homogeneous grains of dimensions of about 20-30 nm. The thickness of the film with one spin-coating was estimated to 200-400 nm by SEM.

### Opto-electrochemical properties

The oxide ( $\text{MnCo}_2\text{O}_4$ ) thin-film electrodes exhibited a reversible change in the absorbance at 400-800 nm, between 0 V and +0.8 V (vs. Ag/AgCl), which shows that an electrochromism could be occurred in this condition. Further more, it was found that the change in the absorbance of the  $\text{MnCo}_2\text{O}_4$  thin-film at 500nm was depended on the  $\text{HPO}_4^{2-}$  concentration. Figure 1 shows the change in the absorbance at 500 nm for the  $\text{MnCo}_2\text{O}_4$  electrode as a function of  $\text{K}_2\text{HPO}_4$  concentration. The absorbance at 500nm of the film at +0.8V was almost linear to the logarithm of the  $\text{HPO}_4^{2-}$  concentration between  $1.0 \times 10^{-6}$  and  $1.0 \times 10^{-2}$  M. The sensor responded reversibly and the 90% response time, when the electrode potential was changed from +0.80 to 0 V vs. SCE at  $1.0 \times 10^{-2}$  M, was about 40 s at room temperature. Among the spinel-type oxide thin-films tested, the  $\text{MnCo}_2\text{O}_4$ -system showed the best  $\text{HPO}_4^{2-}$  sensing performance. The sensitivity, the slope for absorbance vs.  $\text{HPO}_4^{2-}$  concentration, for the  $\text{MnCo}_2\text{O}_4$  based element was as high as ca.  $-2.72 \times 10^{-2}$  Abs/decade, which was almost the same value ( $+2.66 \times 10^{-2}$  Abs/dec.) of that for the NiO-based element [4]. On the other hand, the sensitivities of  $\text{NiCo}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$ -based elements were as low as  $+1.90 \times 10^{-3}$  and  $+1.00 \times 10^{-4}$  (Abs/dec.), respectively. While, the  $\text{Co}_2\text{CrO}_4$  and the  $\text{Ni}_2\text{CrO}_4$  based elements showed poor stability. It was further found that the slope for the  $\text{MnCo}_2\text{O}_4$  based element was completely opposite in sign from those of the other oxide based elements, which seems to show the different anodic electrochromic properties between the  $\text{MnCo}_2\text{O}_4$  based electrode and  $\text{HPO}_4^{2-}$ . The  $\text{MnCo}_2\text{O}_4$ -based element also showed high selectivity to  $\text{HPO}_4^{2-}$ , among the tested anions of  $\text{HPO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ .

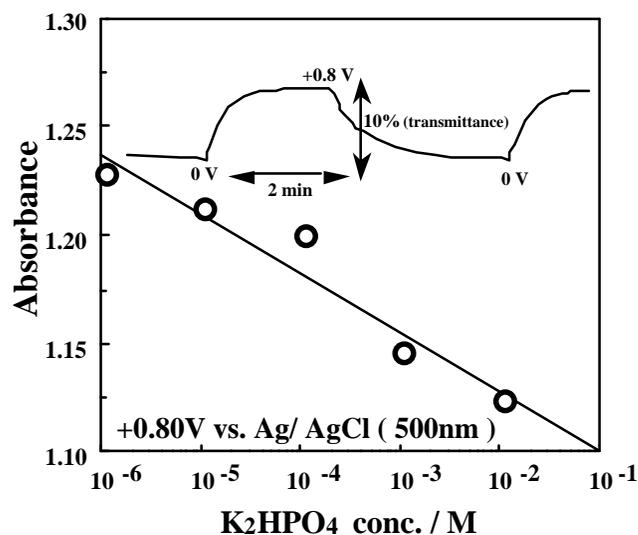


Fig. 1 Sensing performance of the  $\text{MnCo}_2\text{O}_4$  thin-film electrode based electrochromic hydrogen-phosphate ion sensor

## REFERENCES

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